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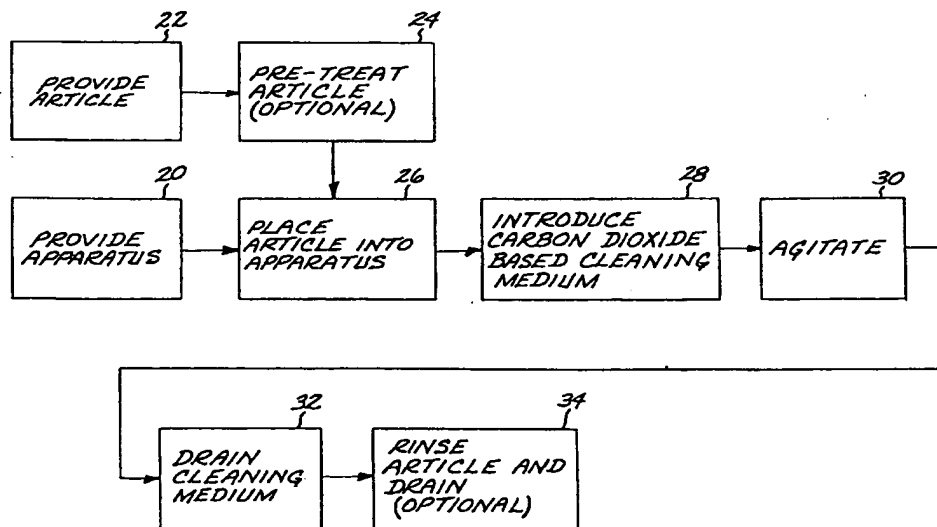
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(54) Title: LIQUID CARBON DIOXIDE CLEANING UTILIZING NATURAL AND MODIFIED NATURAL SOLVENTS



(57) Abstract: An article having soil in contact therewith is cleaned by treating at least a portion of the article with a bio-diesel compound, and agitating the article in contact with dense-phase carbon dioxide to dislodge the soil from the article. The bio-diesel compound may be used in a pre-treatment step, during the agitation step, or both. The bio-diesel compound may be mixed with water and/or a cleaning enzyme.

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LIQUID CARBON DIOXIDE CLEANING UTILIZING NATURAL AND MODIFIED NATURAL SOLVENTS

BACKGROUND OF THE INVENTION

5 This invention relates to the cleaning of articles, and, more specifically, to an approach for improving carbon dioxide cleaning processes.

Conventional organic cleaning solvents historically used in home, industrial, and commercial markets, such as perchloroethylene, CFC-113, 1,1,1 trichloroethane, and petroleum-base solvents, present health and safety risks, because they may be carcinogenic or flammable. The solvents may also be
10 environmentally detrimental, because they are ozone depleting or smog producing. The tightening regulatory controls exercised on the making and using of these solvents has resulted in escalating operating costs and liabilities for all market segments connected to these products.

As a result, alternative cleaning media have been developed and
15 implemented to reduce the health and environmental risks associated with cleaning. Water as a degreasing medium has limitations, because it requires a post-cleaning drying step, and the cleaning process is often lengthy and energy intensive. Water also has poor organic soil solvency, so that additives and vigorous agitation are usually required to remove organic soils. The treatment of
20 the effluent may be expensive, prior to its discharge.

Carbon dioxide is an inexpensive and unlimited natural resource that is non-toxic, non-flammable, non-smog producing, and non-ozone depleting. In its dense phases, both liquid and supercritical, it exhibits solvating properties typical of hydrocarbon solvents. Matter dissolved in dense-phase carbon dioxide may be
25 readily recovered in its concentrated form by gasifying the carbon dioxide. No secondary waste stream is produced such as is associated with the use of conventional solvents. The carbon dioxide does not damage fabric or dissolve common dyes, and its properties make it a good dry cleaning medium for fabrics and garments. It is also a suitable degreasing/cleaning medium for the removal

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of light oils from commercial and industrial parts and components. Dense phase carbon dioxide has been referenced as a cleaning fluid for garments and components in numerous patents, including, for example, US Patents 5,013,366; 5,316,591; 4,012,194; 5,467,492; and 5,267,455.

5 One disadvantage of the dense-phase carbon dioxide is that it is a relatively mild solvent, not readily suitable for heavy oils and greases. In addition, it does not remove hydrophilic soils. As a result, some dense-phase carbon dioxide processes have incorporated additives that either enhance or modify the bulk solvency of the carbon dioxide itself for organophilic soils, or help co-solvate the
10 hydrophilic soils by their ability to carry water into the dense-phase carbon dioxide medium. The use of such additives are referenced in numerous patents, including, for example, US Patents 5,683,977; 5,683,473; 5,676,705; 5,866,005; and 5,789,505.

15 Typical additives used to enhance the organic solvating power of the dense-phase carbon dioxide have been the same compounds that are targeted for displacement because of their harmful nature. Examples include co-solvents such as low alkanes, terpenes, alcohols, ketones, benzene, toluene, xylenes, and chlorinated, fluorinated, or chloro-fluorinated compounds.

20 Also typically, the separation or removal of ionic or water-soluble soils has been enhanced by molecularly engineered surfactants designed to carry water into the carbon dioxide medium. The disadvantage of these additives is their cost, as they require elaborate synthesis. The surfactants may also require the use of the co-solvents discussed above, which defeats the beneficial health and environmental nature associated with the use of the dense-phase carbon dioxide.

25 There exists a need for improving the efficiency of liquid carbon dioxide cleaning processes, which addresses the removal of heavier oils, greases, and hydrophilic soils, while still maintaining the health and environmental benefits of the bulk dense-phase carbon dioxide solvent. The present invention fulfills this need, and further provides related advantages.

30

SUMMARY OF THE INVENTION

This invention provides a method and apparatus for dense-phase carbon

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dioxide cleaning of articles. The approach of the invention retains good effectiveness in removing particulate soils from the articles, and has increased effectiveness in removing grease, oil, and hydrophilic soils as compared with the use of only the dense-phase carbon dioxide. The approach makes use of natural and modified natural additives with good solvating properties. The additives are environmentally friendly, non-toxic, biodegradable, and free of sulfur and aromatics. They may be rinsed with water and form stable emulsions with other phases such as water, mineral spirits, alcohols, and some terpenes. The additives may be used in conjunction with known dense-phase carbon dioxide cleaning procedures.

In accordance with the invention, a method for cleaning an article comprises the steps of providing an article having soil in contact therewith, treating at least a portion of the article with a bio-diesel compound, and contacting the article with dense-phase carbon dioxide to dislodge the soil from the article. Optionally, the article may be rinsed to remove the bio-diesel compound, if it is present after contacting is complete.

"Bio-diesel compounds" are a recognized class comprising alkyl monoesters of vegetable oils, preferably the methyl esters of vegetable oils. Examples of suitable vegetable oils are safflower, sunflower, canola, and soybean oils. The bio-diesel compounds are fully compatible with dense-phase (liquefied or supercritical) carbon dioxide. The term "bio-diesel" originates in an unrelated use of such compounds as ingredients in synthetic diesel fuel.

The article to be cleaned may be fabric or other articles such as metallic, ceramic, or plastic parts to be degreased and cleaned. The contacting of the bio-diesel compound to the article and the agitating of the article may be accomplished completely or partially serially, or simultaneously, as may be appropriate for particular applications. Thus, for example, the article may be pre-treated with the bio-diesel compound and thereafter placed into a pool of dense-phase carbon dioxide in a pressure chamber and agitated. The bio-diesel compound may instead be added to the pool of dense-phase carbon dioxide in an in-situ treatment. A combination of pre-treatment and in-situ treatment may be used. The pre-treatment may be a general pre-treatment such as soaking, or a localized pre-treatment such as the "spotting" of a fabric. The bio-diesel

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compound may be formed into an emulsion with water and/or enzymes, and used in any of these pre-treatment and in-situ treatment alternatives. The contacting and agitating may be accomplished by any operable approach, such as, for example, the force of liquid jets of the dense-phase carbon dioxide directed into the pool, the bubbling as some of the dense-phase carbon dioxide vaporizes, a tumbling action, stirring of the pool by an impeller, circulation of the carbon dioxide with a pump, and ultrasonic cavitation. Thus, a wide variety of treatment and agitation procedures using the bio-diesel compound are within the scope of the invention.

10 The invention provides an improved approach to cleaning processes utilizing dense-phase carbon dioxide as a cleaning medium. The approach addresses the use of specific natural (e.g., enzyme) and modified natural additive (e.g., bio-diesel) compounds that enhance the cleaning efficiency and solvating power of the dense-phase (liquid) carbon dioxide. The function of the bio-diesel
15 compound, alone or in conjunction with additives such as water and/or enzymes, is to solvate and mobilize organics such as oils and greases, as well as hydrophilic particulate soils, so that they may be more readily dislodged from the article being cleaned by the agitation of the dense-phase carbon dioxide. These additives, alone or as carriers of enzymes and/or water, are environmentally friendly, non-toxic,
20 biodegradable, and free of sulfur or aromatics. The method of the invention enhances the effectiveness of the liquid carbon dioxide cleaning medium to remove heavy oils, greases, and hydrophilic soils, while it retains its health and environmentally benign properties as a solvent. Other features and advantages of the present invention will be apparent from the following more detailed
25 description of the preferred embodiment, taken in conjunction with the accompanying drawings, which illustrate, by way of example, the principles of the invention. The scope of the invention is not, however, limited to this preferred embodiment.

BRIEF DESCRIPTION OF THE DRAWINGS

30 Figure 1 is a block flow diagram of a preferred embodiment of a method according to the invention;

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Figure 2 is a schematic system diagram of an apparatus used in the method of Figure 1; and

Figure 3 is a representation of a chemical reaction used to produce a bio-diesel compound.

5

DETAILED DESCRIPTION OF THE INVENTION

Figure 1 depicts a preferred approach for practicing the invention. An apparatus is provided, numeral 20. The apparatus may be of any operable type to accomplish the remaining steps of the process, and Figure 2 depicts one embodiment of a preferred apparatus 40 most suitable for commercial fabric-cleaning operations.

10 The apparatus 40 includes a cleaning chamber 42 having a pressure vessel 44 and a pressure door 46 that seals to the pressure vessel 44. The cleaning chamber 42 is designed to withstand the internal pressures utilized in the subsequent steps, typically in the range of about 550 pounds per square inch (psi) to about 1000 psi, preferably about 700-800 psi, and is made of steel. A
15 perforated basket 48 with openings therein is supported within the cleaning chamber 42, with an open end facing the pressure door 46 so that articles may be placed into or removed from the perforated basket 48 when the pressure door 46 is open. In the illustrated embodiment, the pressure vessel 44 and the perforated
20 basket 48 are cylindrically symmetric about a cylindrical axis 50.

Dense-phase carbon dioxide cleaning medium is delivered to the interior of the cleaning chamber 42 by one or more manifolds 52. Additives are mixed with the dense-phase carbon dioxide, as will be discussed subsequently. Each manifold 52 has one or more jet orifices 54 therein through which the dense-phase
25 carbon dioxide flows. The jet orifices 54 are preferably positioned so that the flow of cleaning medium from the jet orifices 54 is aimed into the interior of the perforated basket 48 through the openings therein and thence around the articles being cleaned.

In operation of the apparatus 40, the dense-phase carbon dioxide is pumped
30 through the manifolds 52 and into the cleaning chamber 42 by a main pump 56 operating through appropriate valves 58 and 60. The dense-phase carbon dioxide

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cleaning medium is initially pumped to a preset depth within the cleaning chamber 42 to form a pool of the liquefied cleaning medium. Upon reaching the desired pool depth, additional dense-phase carbon dioxide is forced through the jet orifices 54 to agitate the pool and the articles therein.

5 After passing through the cleaning chamber 42, the dense-phase carbon dioxide cleaning medium flows to a lint trap 62, which filters solid matter from the cleaning medium. (The lint trap 62 may be omitted where non-fabric articles are cleaned.) A valve 66 permits the dense-phase carbon dioxide to be routed to
10 a more extensive filter train 68, to a condenser 70 having a refrigeration system 72, and back to the inlet side of the main pump 56 through a valve 74. In a "bypass" setting, the valve 66 permits drained dense-phase carbon dioxide to be recovered.

 Liquefied cleaning medium is supplied to the main pump 56 from a storage tank 76, operating through the valve 74. Optional additives to the liquefied
15 cleaning medium to be discussed subsequently, such as water or enzymes, are supplied on the inlet side of the main pump 56 from an additive supply 78 through an additive pump 80.

 Cleaning medium may also flow from the cleaning chamber 42 back to the inlet side of the main pump 56 through a drain line 82 operating through the valve
20 74, during the "drain" portion of the process.

 The apparatus 40 further includes a vent valve 84 permitting the cleaning chamber 42 to be vented to atmosphere. A return path for gaseous carbon dioxide through a compressor 86 to the condenser 70 or to the storage tank 76 is provided with appropriate valves 88, 90, and 91.

25 During cleaning of articles, soluble non-particulate soil is dissolved into the cleaning medium. To separate the soluble non-particulate soil from the cleaning medium, a distillation column 92 with appropriate valving 94 and 96 is provided. The distillation is typically performed off-line, when the cleaning chamber 42 is not in use for cleaning articles.

30 This apparatus 40 is designed primarily for cleaning fabrics but may be used to clean other articles as well. The apparatus is ordinarily optimized for the type of article to be cleaned.

 In a typical cleaning cycle, the material to be cleaned is placed into the

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perforated basket 48 within the cleaning chamber 42, and the pressure door 46 is closed. The valve 91 is opened, and the pressure between the storage tank 76 and the cleaning chamber 42 is equalized. Valve 74 is in a "chamber" position, and fluid from the storage tank 76 is pumped into the cleaning chamber 42 by the main pump 56 through valve 58 (in a "chamber" position"), until the chamber 42 reaches a desired liquid level. Valves 88 and 90 are closed at this time, and a recirculating loop is established through the lint trap 62, the filter train 68, the condenser 70, and back to the main pump 58. The main pump 58 delivers the necessary flow and pressure drop of dense-phase carbon dioxide (and additives, if present) across the orifices 54 to agitate the load to be cleaned by a flow of dense-phase carbon dioxide. At the end of the agitation cycle, valves 88 and 90 are opened, valve 58 is switched to "drain", and valve 66 is switched to "bypass". The liquid phase carbon dioxide is drained and recovered back from the cleaning chamber 42 to the storage tank 76 by the main pump 56, through the drain line 82 and valve 74 (that is now in the "drain" position). At this point, the cleaning chamber 42 contains the load that has been cleaned, and gaseous carbon dioxide. The cleaning chamber 42 is decompressed to atmospheric pressure after the gas compressor 86 recovers the carbon dioxide vapors back to the storage tank 76. Residual gaseous carbon dioxide is vented out through the vent valve 84, the pressure door 46 is opened, and the clean load is removed.

The method of the present invention may be performed with this exemplary apparatus 40 when it is applied to the cleaning of articles such as fabrics or garments, but it is not limited to this apparatus. For example, other types of contacting and agitation devices such as an impeller to agitate the liquid pool in the cleaning chamber 42, an ultrasonic excitation transducer to produce cavitation of the liquid pool, or any of the other techniques discussed herein may be used.

Returning to Figure 1, an article to be cleaned is provided, numeral 22. The article may be of any operable type and configuration, as long as it fits within the perforated basket 48. One preferred application of the present invention is the cleaning of fabric articles such as clothing, and another preferred application is the cleaning and degreasing of parts and components.

There are several operable approaches to performing the cleaning of the

articles using the present invention. In one approach, the article is optionally pre-treated, numeral 24. In the pre-treatment, the article is contacted with a pre-treatment fluid. The contacting may comprise, for example, a spot contacted with the pre-treatment fluid or a submersion and soaking in the pre-treatment fluid.

- 5 The article is maintained in contact with the pre-treatment fluid for a period of time, typically about 1 minute to about 24 hours, preferably about 1 minute to about 60 minutes, to permit the pre-treatment fluid to solubilize any non-particulate soils fixed to the article.

The pre-treatment fluid, where used, preferably comprises a bio-diesel compound. Bio-diesel compounds are alkyl monoesters (specifically, the methyl and ethyl esters) of vegetable oils or fats, preferably the methyl esters of vegetable oils. Examples of suitable vegetable oils are rapeseed, safflower, sunflower, canola, and soybean oils. Bio-diesel compounds may be prepared from used fryer cooking oil, in a re-use of this waste product. Each of the vegetable oils is made up from glycerides derived from many different carboxylic acids, but each oil has its characteristic composition that does not differ substantially from sample to sample. Bio-diesel compounds are obtained by a reaction of transesterification where the glycerine molecule in the raw vegetable oil is replaced by methanol or ethanol as indicated in the reaction depicted in Figure 3, where R, R1, and R2 are saturated or unsaturated long-chain fatty acids. In practice, the chemical reaction of Figure 3 may be accomplished by mixing the vegetable oil with methanol (or alternatively, ethanol) in the presence of potassium hydroxide, then allowing the mixture to settle. The bio-diesel compound is decanted from the top of the reactor, leaving the heavier glycerine in the bottom. This transesterification reaction is referenced in Robert T. Morrison, Organic Chemistry, published by Allyn & Bacon, Inc., 1966, at page 686.

The bio-diesel compounds have the advantages that they have low viscosities, have low vapor pressures, have densities similar to that of liquefied carbon dioxide, are biodegradable, are non-toxic, are free of sulfur and aromatics, and have a relatively high Kaufling-butanol value of about 60 (compared with perchloroethylene, which is about 90), indicating that they are good organic solvents. They are water rinsable and readily form emulsions with water, mineral spirits, alcohols, and some terpenes. They are compatible with dense-phase

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carbon dioxide, having about the same specific gravity of 0.9.

The bio-diesel pretreatment fluid may optionally be mixed with other components, such as water and/or cleaning enzymes. Enzymes are proteins that speed up (catalyze) a reaction that involves the making or breaking of a covalent bond. Enzymes act by lowering the temperature under which a given bond is unstable. Numerous examples exist where well-defined molecules speed up reactions between other molecules, but not all enzymatic reactions are specific. For example, various enzymes that break down proteins into their amino acids are only specific in the sense that they break down the peptide bond. Enzymes typically function in aqueous medium and have been used for a number of years in cleaning processes and in the formulations of many soaps and detergents. Some examples for the use of formulations containing enzymes are spotting compounds that help remove protein-based stains (such as blood) from garments, and detergents that have specific enzymes to help remove fat and oil stains in home laundry. More recently, enzymes have been used in aqueous cleaners to promote the degreasing of parts and components. However, enzymes are typically not soluble or readily miscible in a dense phase carbon dioxide solvent, and a "carrier" compound, here the bio-diesel compound, is needed to facilitate their introduction into a dense-phase carbon dioxide process.

Any operable relative amounts of the bio-diesel compound and the other components may be used. Preferably, the bio-diesel compound, or a mixture of the bio-diesel compound with enzymes or water in any ratio, is present in the dense-phase carbon dioxide in an amount of from about 0.01 to about 5 percent by volume. Lesser amounts are ineffective, and greater amounts are wasteful and lead to residual contamination of the cleaned article with the bio-diesel compound that may necessitate its removal. The pretreatment, if used, may be performed within the cleaning chamber 42 or in a separate container.

The article, which optionally may be pretreated in step 24, is placed into the cleaning apparatus 40, numeral 26, in this preferred case into the perforated basket 48 of the cleaning chamber 42. The pressure door 46 is closed and sealed. A cleaning medium is introduced into the sealed cleaning chamber 42 to form a pool therein, numeral 28, by pumping the cleaning medium from the storage tank 76 using the main pump 56 in the manner described previously. The pool

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preferably partially or fully covers the article in the perforated basket 48.

The cleaning medium comprises the liquefied carbon dioxide with the addition of one or more of the bio-diesel compounds discussed above. The cleaning medium introduced in step 28 may be the same composition as the pre-treatment cleaning medium used in step 24, or a different bio-diesel-containing medium may be used. Other additives may be added as well, such as the water and/or enzymes discussed earlier. The prior discussion of these various materials is incorporated herein. The total amount of additives is typically from about 0.01 to about 5.0 percent, with a preferred range of about 0.1 to about 1.0 percent, of the total of the carbon dioxide and the additives.

The pool and the article therein are agitated, numeral 30. The agitation is accomplished in the illustrated apparatus 40 by the action of the cleaning medium pumped through the manifold 52 and the liquid jet orifices 54. For this purpose, the liquid jet orifices 54 are directed toward the interior of the perforated basket 48 through the openings therein, to impinge upon the articles to be cleaned therein.

The agitation is continued for a period of time sufficient to dislodge particulate soil adhered to the article, and to solubilize and remove non-particulate matter such as oils, grease, and hydrophilic soils. This agitation time varies according to the nature of the article, the dirtiness of the article, and other factors, but is typically from about 5 to about 30 minutes. Agitation may be accomplished by any operable approach, such as the preferred liquid jets, but also hydrodynamic cavitation generated by a propeller, impeller, or blade, circulation with a pump or compressor, ultrasonic cavitation produced by transducers, sonic whistles, or a combination of these techniques.

Upon completion of the agitation, the cleaning medium is drained from the cleaning chamber 42, numeral 32. Optionally, the article may be rinsed, numeral 34, by introducing a rinsing medium such as neat liquefied carbon dioxide into the cleaning chamber 42 and agitating the articles with the un-modified liquefied carbon dioxide. This step is performed if the cleaning medium was used with additives, and it is desirable to remove those additives completely from the article before the article is used. For example, if the article is a fabric such as clothing, and the cleaning medium contained some bio-diesel compound, it is usually

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desirable to rinse out the bio-diesel compound with un-modified liquefied carbon dioxide. In other cases, such as the degreasing of articles, it may be desirable to leave the bio-diesel compound in place as a temporary corrosion-resistant coating on the articles. After the completion of the rinsing step 34, the rinsing medium
5 is drained out of the cleaning chamber 42.

After recovery of most of the liquid and gaseous carbon dioxide back to storage, the residual pressure within the cleaning chamber 42 is vented to atmospheric pressure using the vent valve 84, and the articles are removed from the cleaning chamber 42. Any remaining carbon dioxide evaporates during this
10 venting and removal, leaving the articles dry and clean upon removal from the cleaning chamber.

The following examples illustrate the application of the invention, but should not be interpreted as limiting of the scope of the invention in any respect.

Example 1

15 A load of stainless steel metal parts was treated with various greases, such as CRC Industries No. MSDS SL3310, 3160, 3131, 3141, and Exxon L/M 487211, and with thread cutting oil type C10326 made by W.H. Harvey. The parts were placed into a 12 gallon capacity liquid carbon dioxide cleaning chamber 42.

20 Sufficient liquid carbon dioxide was introduced into the chamber to submerge the load. In some cases, a bio-diesel compound, commercially marketed by the Charbon Group, Huntington Beach, CA as SSW-1000, was added to the chamber 42 in an amount of 0.1 percent, 0.5 percent, 1.0 percent, or 2.0 percent of the total of the carbon dioxide and the bio-diesel compound. The liquid
25 carbon dioxide (and bio-diesel compound, where present) cleaning medium was agitated for 10 minutes at temperatures in the range of 0-85°F, using a cavitating blade and propeller, to accelerate the removal of grease and oil. The solvent was then drained, the chamber was decompressed, and the parts were removed and examined for the presence of visual and tactile residue.

30 Where no bio-diesel compound was used, only the mineral oil component of the greases was removed, and the drawing soaps and other additives in the

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greases remained to contaminate the parts in the form of a tough film-like coating. The thread cutting oil remained as a sticky residue on the parts.

Where the bio-diesel compound was present, the removal of grease and oils was improved in all cases. Some improved removal of grease and oil was observed for 0.1 percent bio-diesel compound, but complete grease removal required at least about 1.0 percent bio-diesel compound. The cutting oil residue was removed at 0.2 percent bio-diesel compound and above. After treatment, the parts were dry, and there was no evidence of residual bio-diesel compound on the parts even for 2.0 percent bio-diesel compound additive.

10 Example 2

A load of stainless steel parts was treated with a polishing compound consisting of heavy waxes and aluminum powder in the 20-40 micrometer range. The load was pre-treated (step 24) for 30 minutes in bio-diesel compound of the same type used in Example 1.

15 After pre-treatment, and without drying, the load was placed into the same cleaning chamber used in Example 1, and treated in the same manner as described for Example 1 (steps 26, 28, 30, and 32).

Where no bio-diesel compound was used in either the pretreatment or the agitation steps, no substantial removal of polishing compound was observed.

20 Where bio-diesel compound was present, there was some removal of the polishing compound even for 0.1 percent concentration of the bio-diesel compound. Full removal required 1 percent of bio-diesel compound or more.

The example was repeated without a pre-treatment, for concentrations of the bio-diesel compound of 0.1 percent, 0.5 percent, 1.0 percent, 2 percent, and 25 5 percent in the liquefied carbon dioxide used in steps 28 and 30. Full removal of the polishing compound required a 5 percent concentration of the bio-diesel compound, substantially greater than the 1.0 percent required where a pre-treatment is employed. When the 5 percent concentration of the bio-diesel compound was used, it was necessary to conduct a post-agitation rinse (step 34), 30 because there was a light film of bio-diesel compound remaining on the parts after agitation and draining.

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Examples 1-2 demonstrate that the use of the bio-diesel compound enhances the cleaning of the parts. Example 2 shows that the pre-treatment lowers the amount of the bio-diesel compound required in the subsequent treatment and agitation, reducing the need for post-drain rinsing.

5 Example 3

 A load of stainless steel parts was dipped into a saturated salt water solution, removed, and allowed to dry. The load was then placed into the cleaning chamber discussed in Example 1. A solution of liquid carbon dioxide and bio-diesel compound/water (0.5 percent bio-diesel compound plus water, 1:1 volume
10 ratio of bio-diesel compound to water) was introduced into the chamber and agitated for 10 minutes to solubilize the salt and remove it from the part. The treatment was under the same conditions as discussed for Example 1. The chamber was then drained and the parts were removed and inspected.

 The same experiment was performed without any bio-diesel compound and
15 water present.

 Where there was bio-diesel compound and water present in the cleaning medium, the salt was removed. Where there was no bio-diesel compound and water present in the cleaning medium, the salt was not removed.

Example 4

20 The same polishing compound used in Example 2 was applied to a load of stainless steel parts, and the load was placed into the cleaning chamber discussed in Example 1.

 A solution of liquid carbon dioxide and bio-diesel compound/water/Bacto-
zyeme enzyme (0.5 percent of bio-diesel compound/water/Bacto-zyeme, with a ratio
25 of 1:1:1 by volume bio-diesel compound:water:Bacto-zyeme) was introduced into the chamber and agitated for 10 minutes under the conditions discussed in Example 1, except that the temperature was in the range of 40-85°F. Bacto-zyeme, discussed in MSDS 1113, is a natural multifaceted enzyme agent having a complex non-bacterial organic formulation that promotes the penetration and

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emulsification of oily or fatty substances and is marketed commercially by the Charbon Group.

The presence of the water and Bacto-zyme enhanced the degreasing, as compared to a control test where no water and Bacto-zyme were present.

5 Example 5

A load of fabric was spotted with thread cutting oil, the spots were treated with concentrated bio-diesel compound fluid, and the load was placed into the cleaning chamber discussed in Example 1. Liquid carbon dioxide was introduced

- 10 The fluid was drained, the system was decompressed, and the fabrics were removed for evaluation. No residual cutting oil was visible on the fabrics, which were spot free and dry when removed.

- 15 Although particular embodiments of the invention have been described in detail for purposes of illustration, various modifications and enhancements may be made without departing from the spirit and scope of the invention. Accordingly, the invention is not to be limited except as by the appended claims.

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CLAIMS

What is claimed is:

1. A method for cleaning an article, comprising the steps of:
providing an article having soil in contact therewith;
treating at least a portion of the article with a bio-diesel compound; and
contacting the article with dense-phase carbon dioxide to dislodge the soil
5 from the article.
2. The method of claim 1, wherein an initiation of the step of treating
is prior to an initiation of the step of contacting.
3. The method of claim 1, wherein a completion of the step of treating
is prior to an initiation of the step of contacting.
4. The method of claim 1, wherein at least a portion of the step of
treating is performed simultaneously with the step of contacting.
5. The method of any of claims 1-4, including an additional step, after
the step of contacting is complete, of
rinsing the article to remove the bio-diesel compound therefrom.
6. The method of claim 5, wherein the step of rinsing includes the step
of
rinsing the article with the dense-phase carbon dioxide, after the step of
treating has been completed.
7. The method of any of claims 1-6, wherein the article is selected
from the group consisting of a piece of fabric, a metal, a ceramic, and a plastic.
8. The method of any of claims 1-7, wherein the step of treating

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includes the step of
mixing the bio-diesel compound with water.

9. The method of any of claims 1-7, wherein the step of treating includes the step of
mixing the bio-diesel compound with a cleaning enzyme and water.

10. The method of any of claims 1-9, wherein the article is in contact with a pool comprising the dense-phase carbon dioxide during the step of contacting.

11. The method of claim 10, wherein the pool further comprises the bio-diesel compound.

12. The method of any of claims 1-11, wherein the step of contacting includes the step of
directing a flow of the liquefied gas around the article.

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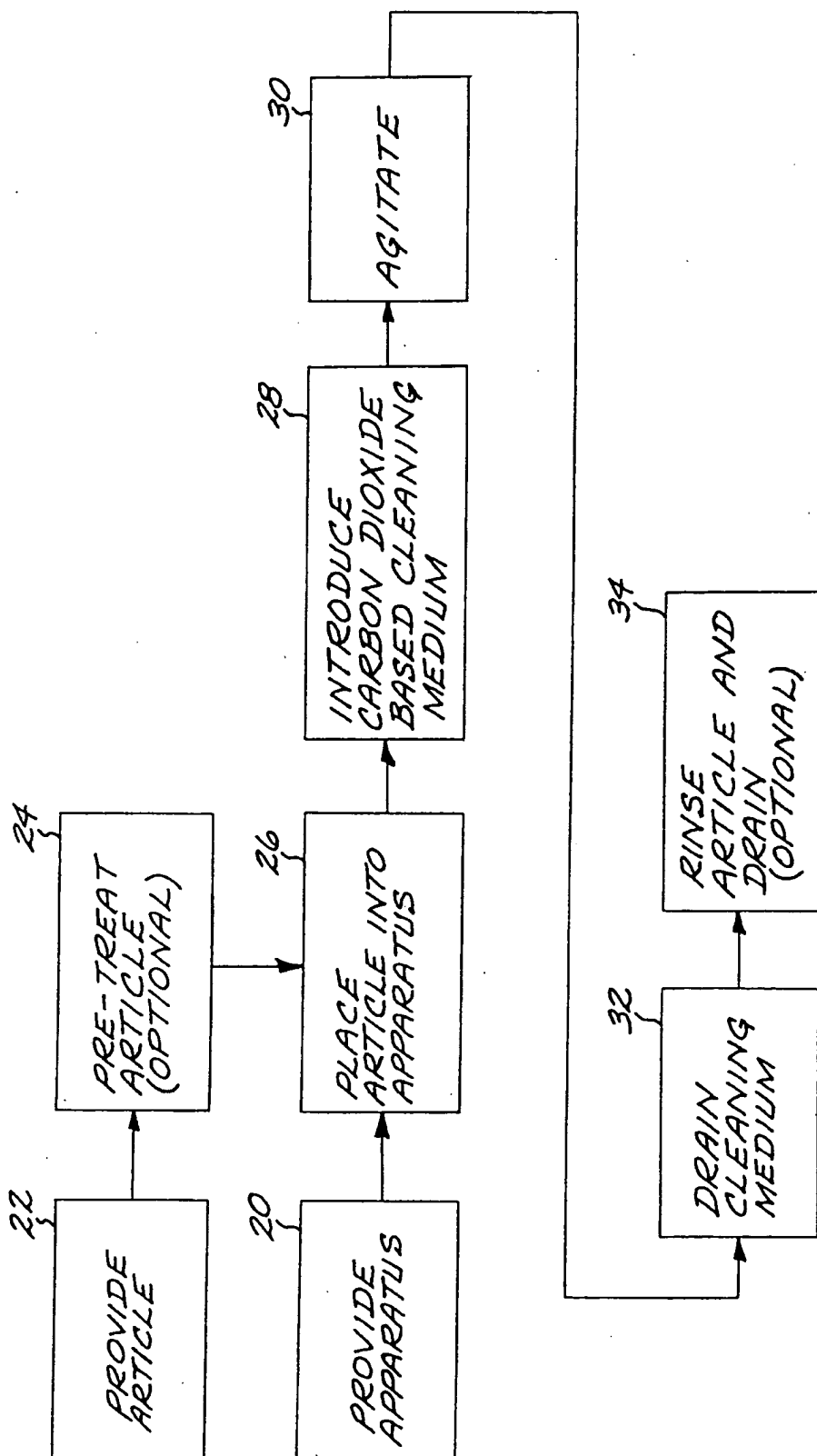


FIG. 1

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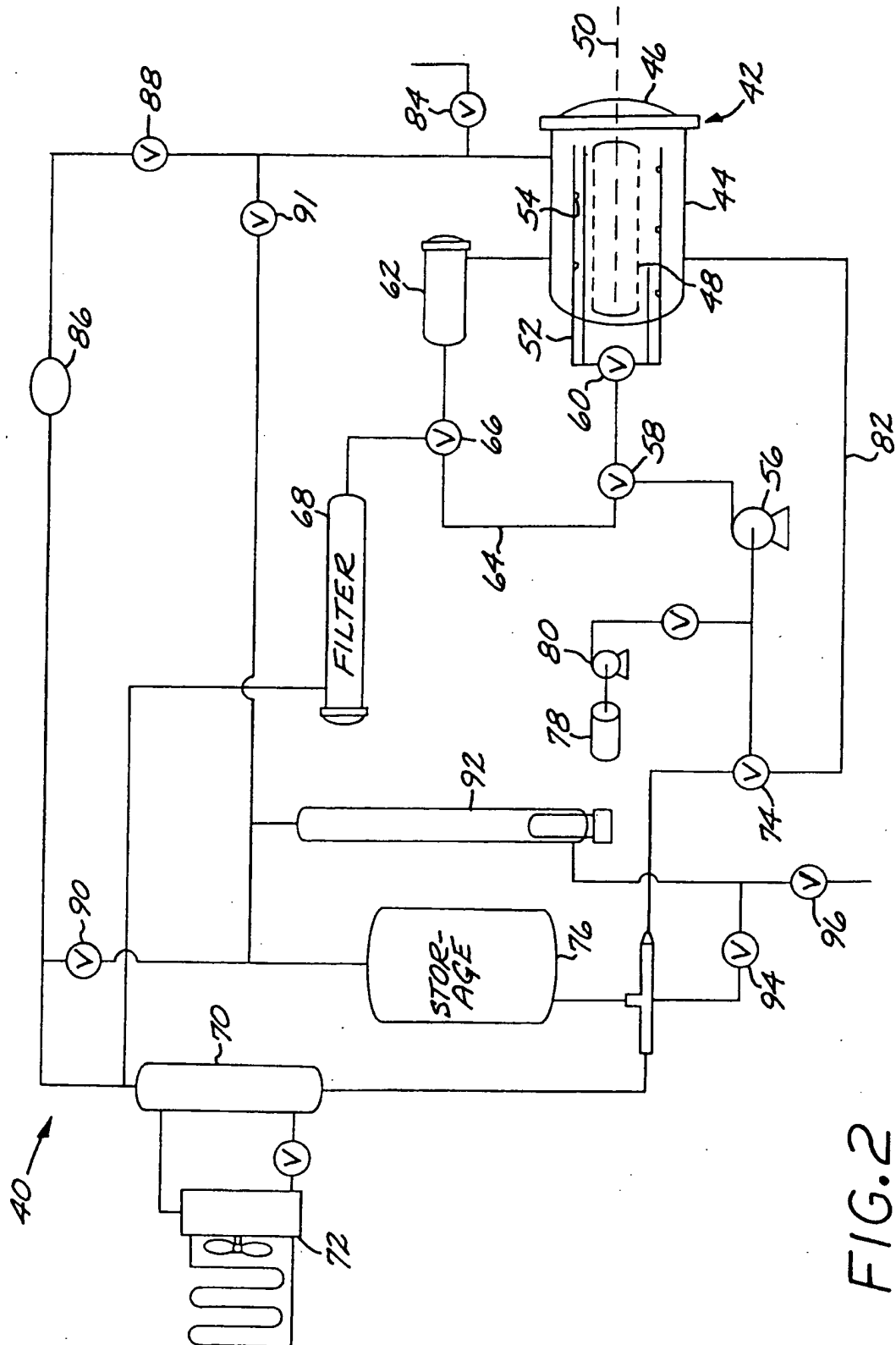


FIG. 2

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FIG. 3

